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Tunable band gap in epitaxial ferroelectric Ho(Mn,Ga)O_3 films

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Ferroelectrics have recently attracted attention as a new class of materials for use in optical and photovoltaic devices. We studied the electronic properties in epitaxially stabilized ferroelectric hexagonal Ho($Mn_{1-x}Ga_x$)O_3 ($x = 0$, 0.33, 0.67, and 1) thin films. Our films exhibited systematic changes in electronic structures, such as bandgap and optical transitions, according to the Ga concentration. In particular, the bandgap increased systematically from 1.4 to 3.2 eV, including the visible light region, with increasing Ga concentration from $x = 0$ to 1. These systematic changes, attributed to lattice parameter variations in epitaxial Ho($Mn_{1-x}Ga_x$)O_3 films, should prove useful for the design of optoelectronic devices based on ferroelectrics. *Published by AIP Publishing.*
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Since the discovery of ferroelectric photovoltaic effects,[1,2] there has been renewed interest in ferroelectric materials.[3–13] Spontaneous electric polarization in ferroelectrics promotes the separation of photoexcited electron–hole pairs. The generated photovoltage can be significantly larger than the bandgap of ferroelectric materials.[4] In principle, this above-bandgap photovoltage can lead to energy conversion efficiencies beyond the maximum values of conventional semiconductor solar cells, in which the photovoltage is limited by the bandgap of the light-absorbing semiconductor. Another unique characteristic of ferroelectric photovoltaics is that the photocurrent direction can be switched by changing the spontaneous polarization direction with the electric field. However, further improvement in ferroelectric photovoltaics has been inhibited by the wide bandgaps of ferroelectric oxides (e.g., $E_g \sim 3.5$ eV in $BaTiO_3$ and ~2.7 eV in $BiFeO_3$) and difficulty in tuning the bandgaps. As such, this has prompted the development of new semiconducting ferroelectric oxides,[9] with bandgaps in the visible light region and that are also largely tunable.

Compared with conventional ferroelectric oxides, hexagonal rare earth manganites (*h*-$RMnO_3$)[14–19] have a distinct advantage for photovoltaic applications. Together with a reasonably large spontaneous polarization ($\geq 5\ \mu C/cm^2$), *h*-$RMnO_3$ shows an intrinsically narrow bandgap based on the partially filled 3*d* electronic states (Fig. 1). Within the bipyramidal crystal field [Figs. 1(b)–1(e)], the Mn 3*d* states are split into two doublets, e_{2g} ($d_{xy}/d_{x^2-y^2}$) and e_{1g} (d_{yz}/d_{zx}), and one singlet a_{1g} ($d_{3z^2-r^2}$). These doublets and singlet form the valence and conduction bands, respectively, giving a bandgap as small as $E_g \sim 1.4$ eV.[20–23] Therefore, light absorption occurs in the visible region, which promises optical and photovoltaic applications using ferroelectric *h*-$RMnO_3$. It is expected that E_g in *h*-$RMnO_3$ could be further tuned simply by using the lattice strain and/or chemical doping [Figs. 1(c) and 1(e)], which is essential for the design of optoelectronic devices.[8–13] However, there have been few reports regarding bandgap tuning in *h*-$RMnO_3$.

Here, we report the large, systematic tunability of bandgaps in epitaxial ferroelectric Ga-doped *h*-$HoMnO_3$ [i.e., *h*-Ho(Mn,Ga)O_3] thin films. As Ga^{3+} ions do not have any *d* electrons, substitution of Mn^{3+} by Ga^{3+} ions can lead to substantial changes in electronic structures (e.g., E_g). On the other hand, Ga doping causes only small changes in the crystal structure[24,25] and will not compromise the ferroelectricity. Thus, *h*-Ho(Mn,Ga)O_3 may emerge as a new semiconducting ferroelectric system that will allow tunable visible light absorption. However, there have been no clear experimental demonstrations of the electronic properties or ferroelectricity of *h*-Ho(Mn,Ga)O_3 systems, mainly due to a lack of high-quality epitaxial thin films.

We grew ~100 nm-thick *h*-Ho($Mn_{1-x}Ga_x$)O_3 ($x = 0$, 0.33, 0.67, and 1) epitaxial films using pulsed laser deposition (PLD) with a KrF excimer laser (wavelength: 248 nm; Lambda Physik). Note that for a large Ga concentration (e.g., $x > 0.2$), Ho($Mn_{1-x}Ga_x$)O_3 has an orthorhombic phase in bulk form.[26] To obtain hexagonal phase in all *x*, we used the epitaxial stabilization technique[15] using substrates with hexagonal symmetry,

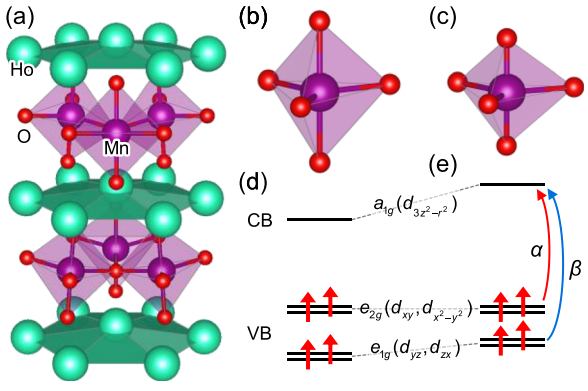

FIG. 1. (a) Crystal structure of hexagonal $HoMnO_3$. (b) Mn-centered trigonal bipyramid and (c) flattened bipyramid, consisting of Mn^{3+} and O^{2-} ions. (d) Schematic representation of the crystal field splitting in MnO_5 trigonal bipyramids. The two doublet states, e_{1g} and e_{2g}, are occupied and form the valence band (VB), whereas the singlet a_{1g} is unoccupied and forms the conduction band (CB). (e) The flattening of the MnO_5 bipyramid can cause the $a_{1g}(d_{3z^2-r^2})$ state to shift to a higher energy, thereby increasing the bandgap, E_g.

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i.e., yttria-stabilized zirconia (YSZ) (111). Ho(Mn,Ga)O_3 has a lattice mismatch [i.e., $(a_{substrate} - a_{bulk})/a_{bulk}$] of $\geq$2.8% with the YSZ(111) substrate, inducing tensile epitaxial strain in the films.[17] We used a substrate temperature of 900 °C and an oxygen partial pressure of 350 mTorr. Sintered ceramic pellets of stoichiometric Ho(Mn,Ga)O_3 were used as PLD targets. After deposition, X-ray diffraction (XRD) measurements were performed using a high-resolution four-circle X-ray diffractometer (D8 Advance; Bruker AXS). The ferroelectric properties of the films were measured using a TF Analyzer (aixACCT) at a frequency of 2 kHz. To reduce the leakage current, ferroelectric measurements were carried out at 200 K using a low-temperature probe station (Desert Cryogenics). Near-normal incidence reflectance and transmittance spectra of the thin films in the photon energy range of 0.1–6.0 eV were obtained using a Fourier-transform infrared (FT-IR) spectrometer (Bruker IFS66v/S) and a grating-type spectrophotometer (CARY 5G) at 0.1–1.2 eV and 0.4–6.0 eV, respectively.

High-quality epitaxial Ho(Mn,Ga)O_3 thin films were obtained under optimized growth conditions. Figure 2(a) shows XRD θ–2θ scans for Ho(Mn,Ga)O_3 films on the YSZ(111) substrate. Only the (0002), (0004), (0006), and (0008) hexagonal reflections of the films were visible, along with substrate peaks. These observations indicated the formation of a pure h-R(Mn,Ga)O_3 phase. Epitaxial growth of the h-Ho(Mn,Ga)O_3 phase was confirmed via XRD reciprocal space mappings [Figs. 2(b) and 2(c)], as well as XRD ϕ-scans, presented elsewhere.[27] From the XRD data, we evaluated the in-plane a and out-of-plane c lattice parameters of Ho($Mn_{1-x}Ga_x$)O_3 films as a function of x [Fig. 2(d)]. Our results showed that the in-plane a lattice (out-of-plane c lattice) increased (decreased) with increasing Ga concentration (i.e., x). We will discuss later how this change in lattice parameters influences the physical properties of Ho($Mn_{1-x}Ga_x$)O_3 films.

We examined the ferroelectric properties of h-Ho(Mn,Ga)O_3 films by measuring the switching current during ferroelectric switching (i.e., $I_{SW} \propto \partial P/\partial t$) and the resulting polarization versus electric field (P–E) hysteresis loops. At room temperature, there was a large leakage current, probably due to an intrinsic narrow E_g and possible oxygen non-stoichiometry. This leakage current prevented higher temperature measurements; thus, the ferroelectric measurements were carried out at 200 K. Figure 3 shows the I_{SW} and P–E hysteresis loops for h-Ho(Mn,Ga)O_3 films. While I_{SW} and P–E hysteresis loops clearly confirmed the ferroelectricity of h-Ho(Mn,Ga)O_3 films, we observed gradual suppression of ferroelectricity (i.e., reduced I_{SW} and smaller remnant polarization) in h-Ho($Mn_{1-x}Ga_x$)O_3 films with increasing x. We did not observe any clear ferroelectricity

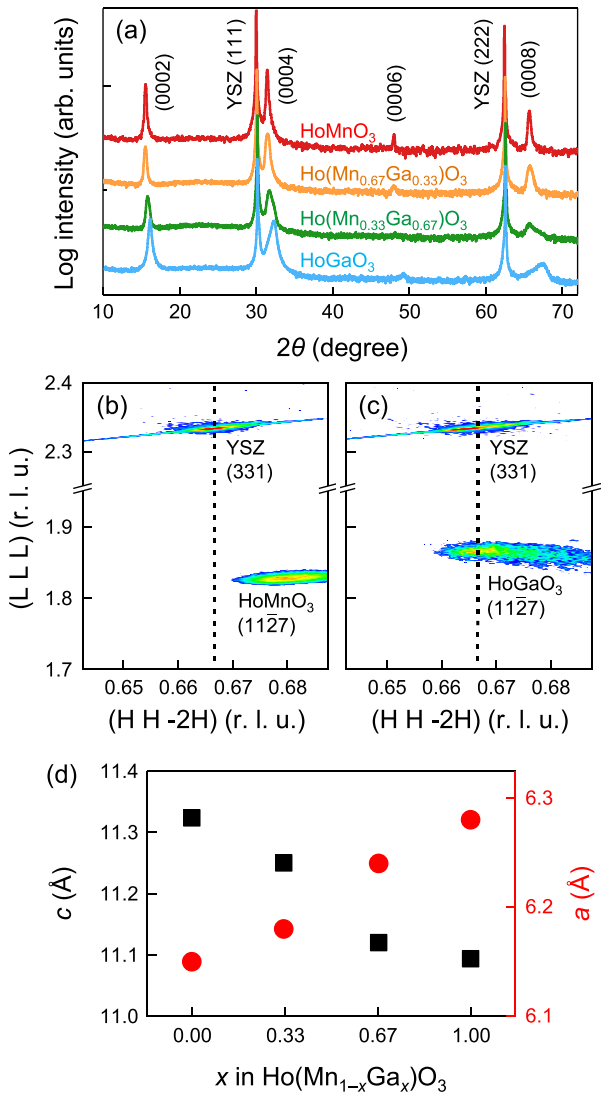

FIG. 2. (a) X-ray diffraction (XRD) θ–2θ scans of h-Ho(Mn,Ga)O_3 films on a YSZ(111) substrate. XRD reciprocal space mapping results for (b) h-$HoMnO_3$ and (c) h-$HoGaO_3$ films around the (331) reflection of the YSZ substrate. (d) Averaged c and a lattice parameters of h-Ho(Mn,Ga)O_3 films obtained from XRD measurements.

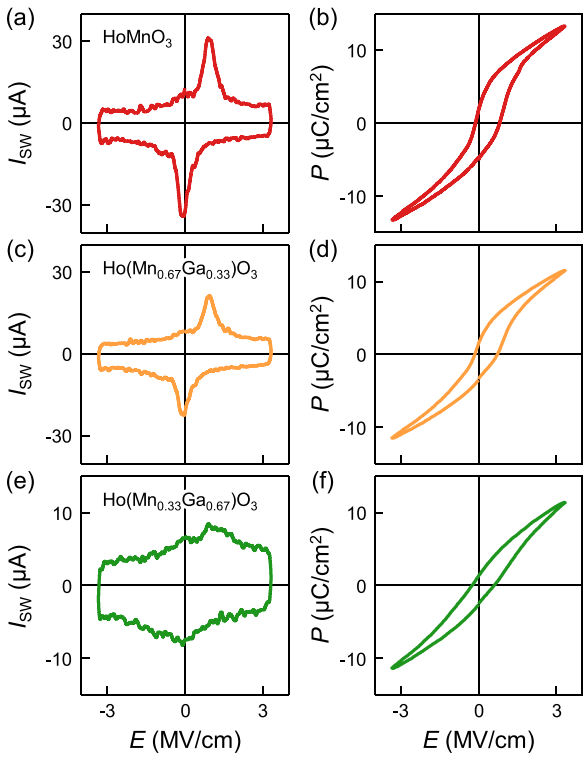

FIG. 3. Switching current (I_{SW}) hysteresis loops and polarization–electric field (P–E) hysteresis loops for (a), (b) $HoMnO_3$; (c), (d) Ho($Mn_{0.67}Ga_{0.33}$)O_3; and (e), (f) Ho($Mn_{0.33}Ga_{0.67}$)O_3 epitaxial films. For these electrical measurements, we selected a Pt(111)/Al_2O_3(0006) substrate with a similar lattice mismatch as the YSZ(111) substrate.[17]

(i.e., I_{SW} and P–E hysteresis loops) in $HoGaO_3$ films (data not shown).

In h-Ho(Mn,Ga)O_3 bulk, a previous XRD study predicted the enhanced ferroelectricity (e.g., higher T_C) by Ga doping.[24] Till date, however, complete P–E loop data have not been available for either bulk or thin films of Ga-doped h-$HoMnO_3$. Our results of I_{SW} and P–E loops indicated that ferroelectricity in epitaxial h-Ho(Mn,Ga)O_3 films does not simply follow the prediction from the bulk, but shows gradual suppression of ferroelectricity by Ga doping. We already mentioned that our epitaxial Ho(Mn,Ga)O_3 films experienced the in-plane tensile strain.[17] As spontaneous polarization in h-Ho(Mn,Ga)O_3 occurs along the c axis of the crystal, the application of tensile strain within the ab plane (i.e., contraction of the crystal along the c axis) will suppress their electric dipole moment and therefore reduce spontaneous polarization. A recent theoretical calculation predicted that ferroelectricity in hexagonal rare earth compounds becomes suppressed with increases in the in-plane a lattice parameter.[25] Thus, the suppressed ferroelectricity by Ga doping can originate from the increased a lattice parameter (or the decreased c lattice parameter) in epitaxial films.

Figure 4 shows the optical conductivity spectra of epitaxial h-Ho(Mn,Ga)O_3 thin films. The epitaxial h-$HoMnO_3$ thin films show two different optical absorption peaks at ~1.7 eV and ~2.2 eV, which we previously assigned to the on-site d-d transitions between the occupied and unoccupied Mn^{3+} orbitals [Fig. 1(d)].[21,22] That is, the optical absorption peak at ~1.7 eV (denoted by α) corresponds to the transition between $e_{2g}(d_{xy}/d_{x^2-y^2})$ and $a_{1g}(d_{3z^2-r^2})$ orbitals, and the peak at ~2.2 eV (denoted by β) corresponds to the transition between $e_{2g}(d_{xy}/d_{x^2-y^2})$ and $a_{2g}(d_{yz}/d_{zx})$ orbitals.[20–22] As mentioned earlier, the occupied $e_{2g}(d_{xy}/d_{x^2-y^2})$ orbital and unoccupied $a_{1g}(d_{3z^2-r^2})$ orbital form the valence and conduction bands, respectively. We estimated E_g of h-$HoMnO_3$ to be ~1.4 eV; thus, most visible light can be absorbed. As Ga^{3+} ions do not have any d electrons, it is possible to systematically control the absorption peaks and E_g by Ga doping. Figure 4 shows that the intensity of the absorption peaks decreased with increasing x, and finally, the peaks disappeared at $x = 1$ (i.e., $HoGaO_3$). Furthermore, the absorption peak shifted significantly to a higher energy, and E_g showed a systematic blue shift from ~1.4 to ~3.2 eV with increasing x in h-Ho($Mn_{1-x}Ga_x$)O_3 films. These results emphasize that substitution of Mn^{3+} by Ga^{3+} ions provides an effective means of controlling the electronic structure and E_g in h-$RMnO_3$.

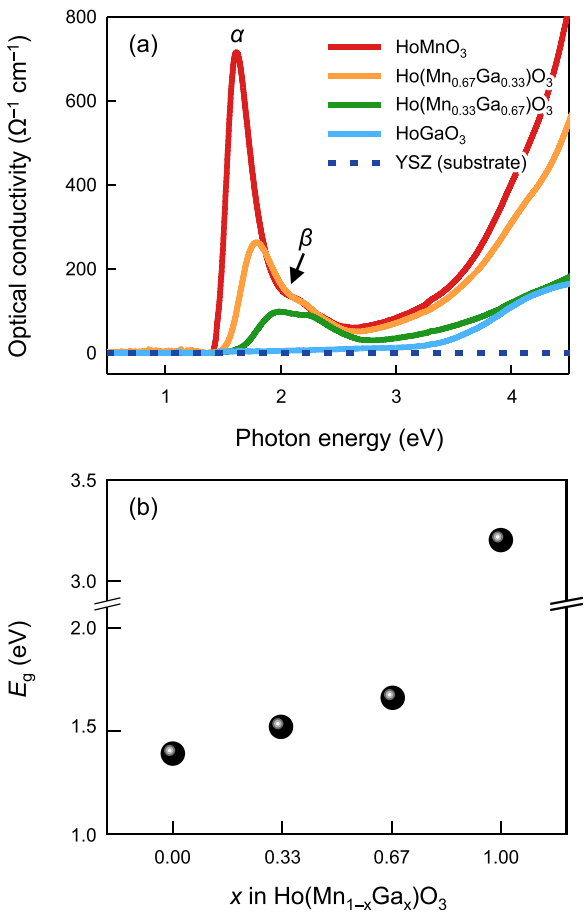

FIG. 4. (a) Optical conductivity spectra of h-Ho(Mn,Ga)O_3 films on the YSZ(111) substrate. The blue dotted line indicates the optical conductivity spectrum of YSZ(111) substrate. (b) Optical bandgap, E_g, of h-Ho(Mn,Ga)O_3 films, estimated from (a).

We can explain the systematic variation of E_g in terms of lattice parameter changes in epitaxial h-Ho($Mn_{1-x}Ga_x$)O_3 thin films. When the out-of-plane c lattice parameter becomes smaller, the MnO_5 triangular bipyramid will flatten out [Fig. 1(c)]. Then, due to the modified crystal field splitting, the energy level of the Mn $d_{3z^2-r^2}$ state increases significantly [Fig. 1(e)], while the Mn $d_{xy}/d_{x^2-y^2}$ state changes negligibly. Ga doping (i.e., increase in x) causes a decrease in the out-of-plane c lattice parameter [Fig. 2(d)], and, as a result, the optical transition α (i.e., from the Mn $d_{xy}/d_{x^2-y^2}$ state to the Mn $d_{3z^2-r^2}$ state) will shift to a higher energy, leading to an increase in E_g. This simple picture well explains the systematic increase in E_g by Ga doping.

We also investigated systematic changes in optical transitions α and β in h-Ho($Mn_{1-x}Ga_x$)O_3 thin films. Figure 5 shows the optical conductivity spectra in the range between 1.0 and 3.0 eV, in which we estimated the relative contributions of α and β using Gaussian fitting. In the undoped h-$HoMnO_3$ thin film, the spectral weight of β was smaller than that of α; with an increase in Ga ions, it became larger. These observations indicated that Ga doping could modify the detailed shape of electronic band structures, which affected the optical transitions. Further work is needed to fully understand the effects of Ga doping on electronic band structures, including the possible depletion of the Mn $d_{xy}/d_{x^2-y^2}$ state with Ga doping. Nevertheless, our results highlight the uniqueness of the h-Ho(Mn,Ga)O_3 system, the electronic structure, and the associated optical properties (especially in the visible light region) of which can be largely tuned by Ga doping.

In summary, we epitaxially stabilized the hexagonal phase of Ho($Mn_{1-x}Ga_x$)O_3 up to $x = 1$ by growing thin films on substrates with hexagonal symmetry. The epitaxial hexagonal Ho($Mn_{1-x}Ga_x$)O_3 thin films showed a semiconducting ferroelectric feature and systematic changes in electronic structures according to the Ga concentration. We explained these systematic changes in terms of lattice parameter variations in the films. The large tunability of E_g in the visible light region makes the Ho($Mn_{1-x}Ga_x$)O_3 system promising

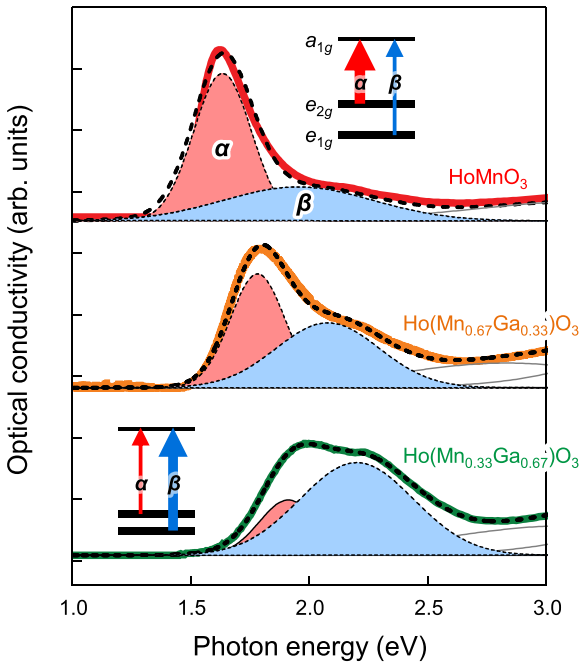

FIG. 5. Enlarged regions of optical conductivity spectra of *h*-Ho(Mn,Ga)O_3 films. Black dashed lines indicate Gaussian fits for optical transitions α and β. Insets show the schematic diagrams for optical transitions α and β, the magnitude of which is represented by the widths of the arrows.

for optical/photovoltaic applications coupled with ferroelectric polarization.[3–13]

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